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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

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PART XXV. MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF THE TIN OXIDES THE DISSOCIATION ENERGY OF SnO

TECHNICAL DOCUMENTARY REPORT No. WADD-TR-60-782, PART XXV

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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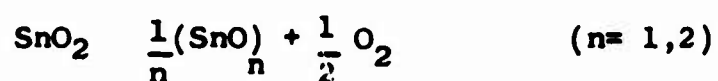
FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-764. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

The authors acknowledge Professor P. Goldfinger's interest in this work. They thank Mr. J. Michelet for assistance with the experiments.

ABSTRACT

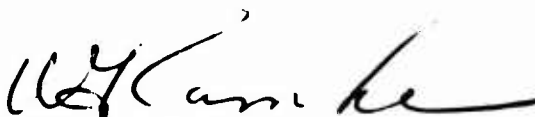
The evaporation of tin oxide SnO_2 and mixtures of tin and tin oxide was studied. The vaporization reactions are



The dissociation energy of SnO is: $D_0^\circ = 126.0 \pm 1.0$ kcal/mole; the polymerization energies are $H_{298}^\circ = 66.8 \pm 4$, 136.5 ± 5 , 207.6 ± 5 kcal/mole for $(\text{SnO})_2$, $(\text{SnO})_3$ and $(\text{SnO})_4$ respectively.

A reinterpretation of the total vapor pressures given in the literature was made.

This technical documentary report has been reviewed and is approved.



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INTRODUCTION

The mass spectrometric study of the vaporization behavior of a number of Group IV_B-Group VI_B compounds has shown the presence of polymeric molecules in the vapor of most of these (1-9). The measurements (4,5) showed these to be present in increasing amounts in going from GeO⁽⁸⁾ to SnO and PbO.

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RTD Technical Report.

It was therefore of interest to investigate and analyse in detail the evaporation behavior of both SnO_2 and $\text{SnO}_2 + \text{Sn}$ not only to derive the thermodynamic properties of these molecules, but also to take their presence into account in the calculation of the dissociation energy of the molecule SnO from total pressure determination^(10,11). Doing so made it possible to explain the discrepancy between the previously generally accepted thermochemical value of the dissociation energy $D_0^\circ(\text{SnO}) = 134 \pm 1 \text{ kcal}$ ^(11,12) and the spectroscopic data, which lead to an upper limit of 130.9 kcal/mole ⁽¹³⁾. The comparison of the data furthermore enable one to show independently that also in SnO the electronically excited E state dissociates to atomic products in their 3P_1 sublevels, the more likely possibility implied by rotational analyses for SnO ⁽¹⁴⁾, SnS ⁽¹⁵⁾, PbO ⁽¹⁶⁾ and PbS ⁽¹⁷⁾.

EXPERIMENTAL.

The mass spectrometer used is a single focussing, 60° sector, 20cm radius of curvature instrument described previously^(18,19). The experimental set-up⁽²⁰⁾ and the principle⁽²¹⁾ of the thermodynamic study of vaporization processes was also given previously.

The commercial SnO samples were used as such. On the basis of the literature data^(11,22), it was considered that in the temperature interval of interest here ($1030\text{--}1200^\circ\text{K}$), this compound has disproportionated to $\text{Sn} + \text{SnO}_2$. The SnO_2 samples were heated at 1000°K under one atmosphere of oxygen for 24 hours prior to evaporation. Several crucible materials tried gave rise to reaction with both SnO and SnO_2 . Quartz was found to be a satisfactory container for SnO_2 while molybdenum and platinum crucibles were used for SnO .

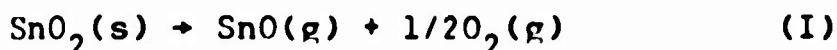
Temperatures were measured both with a Pt-Pt 10% Rh thermocouple and with an optical pyrometer.

RESULTS.

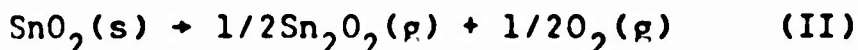
1. Composition of the Vapors.

a) System $\text{SnO}_2(\text{s})$.

The ions characteristic of this system, identified by their mass and isotopic distribution and shown to be produced from neutral species originating from the cell by use of a movable beam defining slit are: O^+ , O_2^+ , Sn^+ , SnO^+ , Sn_2O^+ and Sn_2O_2^+ . Their approximate appearance potentials are given in table 1. From these it was concluded that O^+ , Sn^+ and Sn_2O^+ are fragment ions whereas SnO^+ , O_2^+ and Sn_2O_2^+ are parent ions. The relative intensities of the different ions further indicate that $\text{SnO}_2(\text{s})$ vaporizes according to the reaction



and to a lesser extent according to



b) System $\text{SnO}(\text{s})[(\text{Sn}(\text{l}) + \text{SnO}_2(\text{s}))]$.

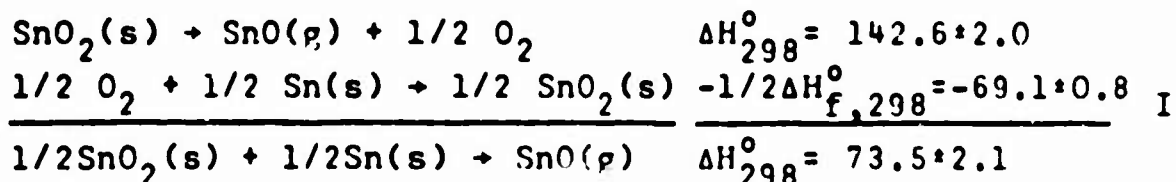
The ionic species characteristic of this system identified as above are: Sn^+ , SnO^+ , Sn_2O^+ , Sn_2O_2^+ , Sn_3O_3^+ and Sn_4O_4^+ . Appearance potentials given in table I, showed again Sn^+ and Sn_2O^+ to be fragment ions and SnO^+ , Sn_2O_2^+ , Sn_3O_3^+ and Sn_4O_4^+ to be parent ions. The vaporization processes for $\text{SnO}_2(\text{s}) + \text{Sn}(\text{l})$ are thus $n/2(\text{SnO}_2(\text{s}) + \text{Sn}(\text{l})) \rightarrow \text{Sn}_n\text{O}_n$, $n = 1$ to 4. In the molybdenum crucibles low ion intensities attributed to $\text{SnO} \cdot \text{MoO}_3$, $(\text{SnO})_2 \cdot \text{MoO}_3$ and $(\text{SnO})_3 \cdot \text{MoO}_3$ were also measured⁽²³⁾. Low intensities at even higher masses were detected but due to the reduced separation at these

higher masses, it was not possible to identify the corresponding ions as due to polymers of SnO or other gaseous molubdates. When a sample of $\text{SnO}_2(\text{s}) + \text{Sn}(\text{l})$ was studied in a tungsten crucible it also gave rise to the formation of several complex molecules⁽²³⁾. Among the ions formed by electron impact from these are SnO.WO_2^+ , $\text{SnO.}(\text{WO}_3)^+$, $(\text{SnO})_2.\text{WO}_3^+$, $\text{SnO.}(\text{WO}_2)_2^+$, $(\text{SnO})_2.(\text{WO}_3)_2^+$ and $(\text{SnO})_3.(\text{WO}_2)_2^+$.

2. Pressures.

The pressures over $\text{SnO}_2(\text{s})$ (table 2.), were calculated from the Hertz Knudsen relation. Samples of known weight were vaporized completely to do so, the intensities of the major species (SnO and O_2) being monitored and integrated with time.

In the $\text{Sn}(\text{s,l}) + \text{SnO}_2(\text{s})$ system, the SnO partial pressures were derived from the calculated energy of vaporization based on the following cycle, in which the value of the dissociation energy of SnO is that to be discussed later.



The numeric values for the thermodynamic functions required in this calculation were taken from the literature⁽²⁴⁻²⁶⁾. The heat of formation of SnO_2 adopted, $\Delta H_{f,298}^0 = -138.1 \pm 0.5$ kcal/mole will be justified in the discussion.

The partial pressures P_n of the polymers (table 3) were obtained from the relation

$$\frac{P_n}{P_1} = \frac{I_n}{I_1} \frac{\sigma_1 \gamma_1}{\sigma_n \gamma_n}$$

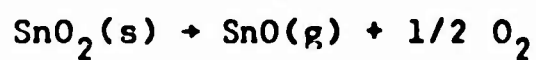
where I is the intensity, σ the relative ionization cross section and γ the relative multiplier efficiency. The σ values were estimated on the basis that the ionization cross section for a dimer is 1.6 times that of the monomer as was shown to hold for several diatomic⁽²⁷⁻²⁹⁾ and dimeric molecules⁽³⁰⁾. Values of atomic ionization cross section were taken from Otvos and Stevenson⁽³¹⁾. Multiplier efficiencies were read from the calibration curve of a multiplier⁽³²⁾ similar to the one used in this work; molecular effects on the first dynode were taken into account⁽³³⁾. The numeric values used are $\sigma = 1, 1.6, 2.1$ and 2.6 , $\gamma = 1.0, 0.7, 0.6$ and 0.7 for SnO , Sn_2O_2 , Sn_3O_3 and Sn_4O_4 respectively.

TABLE 1. Appearance Potentials (in eV).

System	O^+	O_2^+	Sn^+	SnO^+	Sn_2O^+	$Sn_2O_2^+$	$Sn_3O_3^+$	$Sn_4O_4^+$
SnO_2	19.2 ± 1.0	12.2 ± 0.5	13.0 ± 1.0	10.6 ± 0.5	14.0 ± 0.5	9.8 ± 0.5	-	-
$SnO_2 + Sn$	-	-	13.0 ± 1.0	10.4 ± 0.5	13.7 ± 0.5	9.8 ± 0.5	9.8 ± 0.5	9.2 ± 0.5

TABLE 2. Vaporization of $\text{SnO}_2(\text{s})$

Pressures and Enthalpy for the Reaction



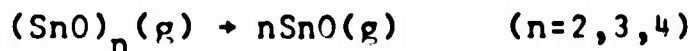
T°K	-log P(atm)			$-\Delta \frac{G_T^\circ - H_{298}^\circ}{T}$	ΔH_{298}
	SnO	O_2	Sn_2O_2		
1254	7.18(± 0.15)	8.00(± 0.15)	-	64.33	144.7
1269	6.88	7.63	-	64.28	143.8
1290	6.53	7.31	-	64.21	143.0
1321	6.23	6.92	-	64.11	143.3
1367	5.71	6.33	-	63.95	142.8
1403	5.12	5.80	7.00(± 0.30)	63.83	141.0
1413	5.07	5.69	6.79	63.73	141.3
1531	4.10	4.67	5.67	63.39	142.2
1538	3.90	4.53	5.39	63.73	140.9
standard deviation					142.6
total uncertainty					± 1.3

TABLE 3. Partial Pressures over $\text{SnO}_2(\text{s}) + \text{Sn}(\text{l})$

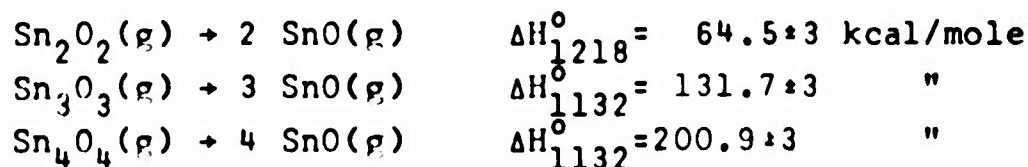
Exp.n°	T°K	- log p(atm)			
		SnO	Sn_2O_2	Sn_3O_3	Sn_4O_4
0901	1153	5.24(± 0.4)	5.17(± 0.5)	5.36(± 0.5)	5.15(± 0.5)
	1194	4.78	4.29	5.03	4.88
0913	1188	4.84	4.40	4.92	4.79
0922	1080	6.09	5.91	6.42	6.42
	1095	5.92	5.68	6.41	6.19
	1091	5.96	5.73	6.24	6.22
	1117	5.63	5.27	5.84	5.57
	1116	5.66	5.44	6.05	5.98
	1171	5.02	4.83	5.48	5.46

3. Thermodynamic Properties of the Sn_2O_2 , Sn_3O_3 and Sn_4O_4 Polymeric Molecules.

The equilibrium constants for the reaction



are given in figure 1. For Sn_2O_2 , equilibrium constants measured at the higher temperatures above SnO_2 were also included. The reaction enthalpies derived calculated by a least square treatment are



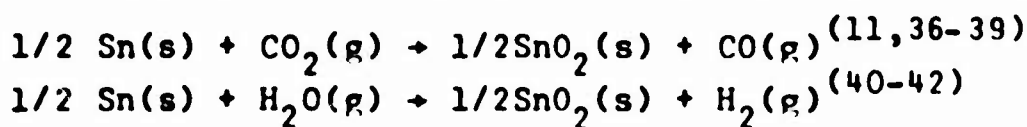
By combining these with the free energies for the corresponding reactions the entropies $S_{1218}^{\circ} = 103.6 \pm 5$, $S_{1132}^{\circ} = 131.6 \pm 6$ and $S_{1132}^{\circ} = 168.6 \pm 6 \text{ e.u.}$ for $(\text{SnO})_2$, $(\text{SnO})_3$ and $(\text{SnO})_4$ respectively, were calculated. By estimating high temperature entropies and heat contents by analogy with a number of tetra, hexa- and octa-atomic molecules⁽³⁴⁾, the polymerization energies and entropies at 298°K were calculated to be $\Delta H_{298}^{\circ} = 66.8 \pm 4 (\text{Sn}_2\text{O}_2)$, $136.5 \pm 5 (\text{Sn}_3\text{O}_3)$, $207.6 \pm 5 \text{ kcal/mole } (\text{Sn}_4\text{O}_4)$ and $S_{298}^{\circ} = 75.0 \pm 6 (\text{Sn}_2\text{O}_2)$, $90.7 \pm 8 (\text{Sn}_3\text{O}_3)$ and $108.1 \pm 8 \text{ e.u. } (\text{Sn}_4\text{O}_4)$.

DISCUSSION.

Different thermochemical values for the dissociation energy of SnO, calculated both from the present data for the vaporization of SnO₂ and from literature data for the vaporization of SnO₂ + Sn^(10,11) or Sn + Ga₂O₃⁽³⁵⁾ mixtures and for the reactions Sn(l) + CO₂ → SnO(g) + CO and SnO₂(s) + CO → SnO(g) + CO₂⁽¹¹⁾ are summarized in table 4.

These were based on cycles analogous to I, in which the dissociation energy of O₂ or the heat of sublimation of tin, ΔH₂₉₈^c = 72.0 kcal/mole⁽²⁶⁾ require no further comments.

The other data are briefly discussed now. The heat of formation for SnO₂(s), ΔH₂₉₈^o(SnO₂(s)) = -138.1 ± 0.5 kcal/mole is the average value calculated from the equilibria:



which were both measured by several authors and treated here by a third law procedure using the free energy functions^(24,25) and heats of formation⁽⁴³⁾, ΔH_{298,f}^o(CO₂) = -94.1 kcal/mole, ΔH_{298,f}^o(CO) = -26.4 kcal/mole and ΔH_{298,f}^o(H₂O) = -57.8 kcal/mole, given in the literature and from the calorimetric value of Humphrey and O'Brian⁽⁴⁴⁾, ΔH_{298,f}^o(SnO₂) = -138.7 ± 0.15 kcal/mole.

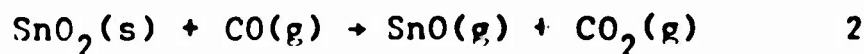
Enthalpies for reaction 1 were recalculated from the apparent pressures measured by Veselowski⁽¹⁰⁾ and Platteeuw and Meyer⁽¹¹⁾ who applied the Knudsen and flow methods respectively and both assumed the vapor over SnO₂(s) + Sn(l) to contain only the molecule SnO. Taking into account the presence of the polymers by use of the relations

$$\begin{aligned} P_K^M &= p(\text{SnO}) + \frac{\sqrt{2}}{K_2} p(\text{Sn}_2\text{O}_2) + \frac{\sqrt{3}}{K_3} p(\text{Sn}_3\text{O}_3) + \frac{\sqrt{4}}{K_4} p(\text{Sn}_4\text{O}_4) \\ &= p(\text{SnO}) + \frac{\sqrt{2}}{K_2} p(\text{SnO})^2 + \frac{\sqrt{3}}{K_3} p(\text{SnO})^3 + \frac{\sqrt{4}}{K_4} p(\text{SnO})^4 \quad (\text{Knudsen}) \end{aligned}$$

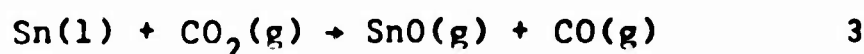
$$P_T^M = p(\text{SnO}) + 2p(\text{Sn}_2\text{O}_2) + 3p(\text{Sn}_3\text{O}_3) + 4p(\text{Sn}_4\text{O}_4) \\ = p(\text{SnO}) = \frac{2}{K_2} p(\text{SnO})^2 = \frac{3}{K_3} p(\text{SnO})^3 = \frac{4}{K_4} p(\text{SnO})^4 \text{ (transport)}$$

where K_n are the equilibrium constants for the reactions $\text{Sn}_n\text{O}_n(\text{g}) \rightarrow \text{SnO}(\text{g})$, the partial pressure of SnO were recalculated. They are summarized in table 4 together with the heats of vaporization of the molecule SnO based thereon.

Platteeuw and Meyer⁽¹¹⁾ also measured the equilibria



and

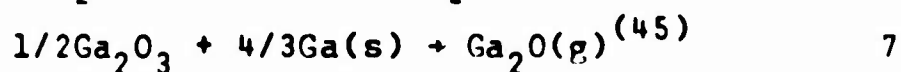
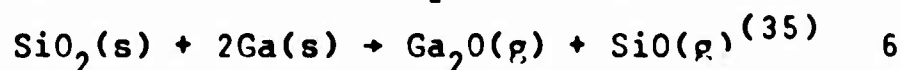
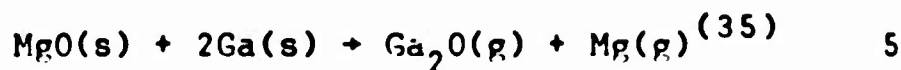


by the flow method. The partial pressure of the monomeric molecule calculated in a similar manner as above from the apparent SnO pressures are also given in table 4, together with the corrected enthalpy change for reactions 2 and 3.

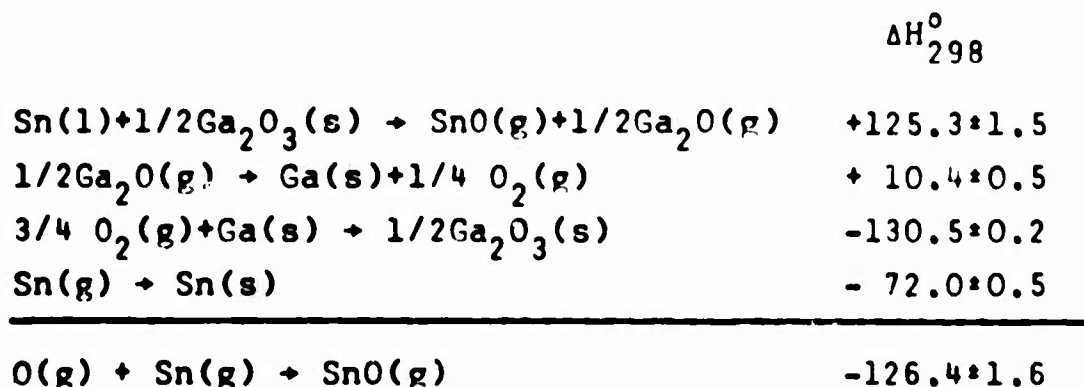
Cochram and Forster⁽³⁵⁾ on the other hand studied the reaction



by the Knudsen technique for which they obtained $\Delta H_{298}^0 = 249.1$ kcal/mole compared to the value $\Delta H_{298}^0 = 236.3$ kcal/mole expected on the basis of the previously accepted dissociation energy of SnO ($D_0^0(\text{SnO}) = 134$ kcal/mole). The latter authors therefore suggest that equilibrium was not established. In fact, reaction 4 leads to a value $D_0^0(\text{SnO}) = 126.3$ kcal/mole if no correction is made for the presence of small amounts of polymers and to $D_0^0(\text{SnO}) = 126.4$ kcal/mole when such correction is made in the same way as above. In the calculation of the dissociation energy from reaction 4, the free energy function of $\text{Ga}_2\text{O}(\text{g})$ used was the same as that adopted by Cochram and Foster⁽³⁵⁾. The heat of formation of $\text{Ga}_2\text{O}(\text{g})$, $\Delta H_{298}^0 = -20.7$ kcal/mole was calculated from the reactions



which, with $\Delta H_{298,f}^\circ(\text{SiO}_2) = -217.5^{(46)}$, $\Delta H_{\text{subl},298}^\circ(\text{Mg}) = 35.6^{(26)}$, $\Delta H_{298,f}^\circ(\text{SiO}_g) = +26.1^{(4)}$, $\Delta H_{298,f}^\circ(\text{Ga}_2\text{O}_3) = -261.05 \pm 0.3^{(47)}$ kcal/mole and the high temperature entropy of Ga_2O_3 recently determined by Pankratz and Kelley⁽⁴⁸⁾, give respectively $\Delta H_{298,f}^\circ(\text{Ga}_2\text{O(g)}) = -20.0, -20.3$ and -21.9 kcal/mole. The average $\Delta H_{298,f}^\circ(\text{Ga}_2\text{O(g)}) = -20.7 \pm 1.0$ kcal/mole was used in the thermochemical cycle:



The average thermochemical value, $D_0^\circ(\text{SnO}) = 125.2 \pm 1$ kcal/mole is in good agreement with two spectroscopic values.

One is based on a continuous absorption at $1931 \pm 6 \text{ \AA}$, attributed to dissociation into $\text{Sn}(^1\text{D}_2) + \text{O}(^3\text{P})^{(13)}$, which gives $D_0^\circ(\text{SnO}) = 124.0$ kcal/mole⁽¹³⁾. The other is obtained from the accurately known convergence limit of the E state at 130.9 kcal/mole⁽¹³⁾. Rotational analysis for SnO , as well as for the analogous molecules, $\text{SnS}^{(15)}$, $\text{PbO}^{(16)}$ and $\text{PbS}^{(17)}$ have shown the latter to correlate most presumably with the $^3\text{P}_1$ sublevels of both Sn and O. On subtracting the corresponding excitation energies from the convergence limit, one obtains $D_0^\circ(\text{SnO}) = 125.6$ kcal/mole. The agreement between this value and the thermochemical one confirms, as in the case of SnS and PbS that the excited E states of these molecules

correlate most probably with the 3P_1 sublevels of the corresponding atoms.

As appears in Table 3 the polymer molecules Sn_2O_2 , Sn_3O_3 and Sn_4O_4 are all of comparable importance in the pressure range investigated here. As discussed above, their presence markedly influences the thermochemical value of the dissociation energy of the monomer calculated from total pressure measurements.

In these polymers, the average SnO-SnO bond as well as the energy required to abstract one monomer from a given polymer are all very close to one another (Table IV). The abstraction energy tends further, as in the other Group IV_B-Group VI_B polymers^(3,5,7,8) towards the heat of sublimation of the monomer, especially if the latter is calculated for the metastable compound SnO for which $\Delta H_{\text{sub},298}^{\circ} = 71.9 \text{ kcal/mole}$ ($\Delta H_{\text{f},298}^{\circ}(\text{SnO,s}) = -67.6 \text{ kcal/mole}^{(49)}$).

TABLE 4. Bond Strenghts in the $(\text{SnO})_n$ Polymers (kcal/mole).

Reaction	ΔH_{298}°
$\text{Sn}_2\text{O}_2(\text{g}) \rightarrow 2\text{SnO}(\text{s})$	66.8 ± 4
$\text{Sn}_3\text{O}_3(\text{g}) \rightarrow \text{Sn}_2\text{O}_2(\text{g}) + \text{SnO}(\text{g})$	69.7 ± 4
$\text{Sn}_4\text{O}_4(\text{g}) \rightarrow \text{Sn}_3\text{O}_3(\text{g}) + \text{SnO}(\text{g})$	71.1 ± 4
$\text{SnO}(\text{s}) \rightarrow \text{SnO}(\text{g})$	71.9 ± 2.5

TABLE 4. Summary of Literature Data for the Dissociation Energy
of the Molecule SnO

Author	Equilibrium	T°K	-logp ^M	-logp(SnO)	ΔH ^o ₂₉₈	D ^o ₀ (SnO)
This work	SnO ₂ (s)→SnO(g)+1/2O ₂ (g)		see table 1.		142.6	126.1±2.1
Veselowski ⁽¹³⁾	1/2SnO ₂ (s)+1/2Sn(l)→SnO(g)	995 ^(a)	6.25	7.15	72.7	
		1166 ^(a)	4.11	5.02	<u>73.2</u> 73.0	126.7±2.5
Platteeuw and Meyer ⁽¹⁸⁾	1/2SnO ₂ (s)+1/2Sn(l)→SnO(g)	1280 ^(a)	2.38	3.75	72.6	
		1400 ^(a)	1.50	2.81	<u>72.8</u> 72.7	127.8±2.5
	SnO ₂ (s)+CO(g)→SnO(g)+CO ₂ (g)	1306 ^(b)	2.32	3.59	73.7	
		1306 ^(c)	3.58	4.17	<u>73.9</u> 73.8	127.3±2.5
	Sn(l)+CO ₂ (g)→SnO(g)+CO(g)	1306 ^(d)	3.02	3.85	72.1	126.2±2.5
Cochram and Foster ⁽³⁰⁾	2Sn(g)+Ga ₂ O ₃ (s)→2SnO(g)+Ga ₂ O(g)	1373	4.08	4.21	249.1	
		1323	4.64	4.75	250.7	
		1273	5.24	5.32	<u>251.8</u> 250.6	125.4±1.6
				average	126.5±2.0	

(a) highest and lowest temperature investigated

(b) n°1, 2 and 3 in table 3, ref.11.

(c) n°4 in table 3, ref.11.

(d) n°5, 6 and 7 in table 3, ref.11.

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